

Application of Modified Bentonites for Arsenite (III) Removal from Drinking Water

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Abstract

Four modified bentonites (La(III), Ce(III), Y(III), Fe(III)) were prepared by ion exchange process to remove arsenite (III) ions from water. The modified bentonites were examined with X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). The rare earth (REE) and Fe(III) ion content in bentonite was higher than the CEC values obtained by ammonium acetate method related to trivalent ions ($2.7 \times 10^{-4} \text{ mol g}^{-1}$). The kinetics, equilibrium time, sorption isotherms and desorption experiments were examined. Lanthanum, yttrium and cerium bentonite can bind similar amount of arsenite(III) ions. Iron-bentonite cannot bind significant amounts of arsenite ions. The active sites and the solubilities of the sorption complex were determined. Arsenite (III) ions sorb in the interlayer space as REEAsO_3 . The solubility of the arsenite complex was two orders of magnitude smaller than that of the phosphate complex. After desorption the eluted amount of arsenite (III) was 55 % related to the sorbed amount of arsenite. The d(001) basal spacing of modified bentonites and that of after sorption and desorption was measured. After the sorption of arsenite ion on lanthanum bentonite, the d(001) basal spacing of montmorillonite was decreased and after desorption an increase in d(001) basal spacing was observed again. Modified bentonites can be used for removing arsenic ions from water.

Keywords

modified bentonite, arsenite (III), rare earth, groundwater, sorption experiments

1 Introduction

One of the most valuable substances on Earth is the clean water suitable for human consumption. The careless treatment and the poisoning of drinking water sources cause an enormous problem around the world.

Arsenic pollution of drinking water is a problem all over the world, mainly those developing countries are affected, where drinking water consist of especially groundwater [1]. Arsenic in water occurs due to anthropogenic effects, but generally it has geogenic origin [2]. In groundwater arsenic occurs as oxyanions; arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}). The limit of arsenic concentration was reduced from 50 $\mu\text{g/l}$ to 10 $\mu\text{g/l}$ [3].

As(III) is more toxic than As(V), and As(III) is more difficult to remove from water than As(V) and generally occurs in water in large quantities. Arsenic can reach the human body by inhalation, ingestion or dermal absorption [4]. Epidemiological studies have presented that

arsenic interact with some hormones in the human body and due to high arsenic concentration in drinking water the risk of bladder, lung, liver, skin and other cancers have increased [2, 5].

Several methods were determined to remove arsenic ions from drinking water, such as adsorption, oxidation, precipitation and ion exchange [6]. Nowadays several metal oxide adsorbents are spread to remove arsenic, for example activated bimetallic oxides [7-9] iron oxide [10-12] alumina [13-15], and other metal oxides [16, 17].

Clay minerals are used for adsorption of pollutants because they are cheap and ubiquitous in nature [18]. The main clay mineral of bentonite is montmorillonite, which is a good sorbent because it has high cation exchange capacity and a large specific surface area. Raw montmorillonite can sorb cations, but not anions, because of the negative charges on the crystal lattice. Therefore, several

methods have been investigated in order to sorb anionic pollutants by montmorillonite [19, 20].

Our aim was to remove arsenic from water with modified bentonites, and to evaluate the As(III) sorption properties of modified bentonites. The kinetics, equilibrium time, sorption isotherms and desorption experiments were examined to determine the characteristic parameters. In this work, calcium bentonite surface was modified with lanthanum (III), yttrium (III), cerium (III), and iron (III) ions, because raw bentonite can sorb cations, but not anions, because of the negative charges on the crystal lattice. Modified bentonites are used for removing arsenite ions from water by adsorption or surface precipitation, a special way of sorption.

These four modified bentonites have been chosen because La-bentonite was used to remove the chemically similar phosphate anion. The idea was taken from the example of the lanthanum modified bentonite Phoslock, invented by CSIRO (Commonwealth Scientific and Industrial Research Institution) in Australia in the mid-1990s. Phoslock decreases phosphate content in water bodies, preventing its re-release for use by algae [21]. Ce- and Y-bentonite are assumed to have similar properties to lanthanum bentonite but they are less expensive. The iron ions are ubiquitous in groundwater. For the application of these sorbents, their interfacial reactions must be known in aqueous media.

Our focus is on As(III) because it is more toxic than As(V), generally more likely to occur in water, and is more difficult to remove from water.

2 Materials and methods

2.1 The characterization of calcium bentonite

Rare earth (REE) bentonites were prepared from natural Ca-bentonite collected in Istenmezeje, Hungary. Elemental analysis of the original Ca-bentonite were measured with EDAX. It has the following composition: 73.29 % SiO₂, 18.71 % Al₂O₃, 1.48 % FeO, 2.29 % CaO and 4.23 % MgO [22]. The X-ray diffraction and thermogravimetric results are: 71 m/m% montmorillonite, 12 m/m% cristobalite / opal CT, 8 m/m% illite, 4 m/m% quartz, 3 m/m% kaolinite, and 2 m/m% calcite. The cation exchange capacity (CEC) of Ca-bentonite was determined by ammonium acetate method [23] and it was 81 meqv / 100 g. The d(001) basal spacing of Ca-bentonite was 1.4769.

2.2 Preparation of trivalent cation exchanged (La, Ce, Y, Fe(III)) bentonites

REE bentonites were prepared by an ion exchange process using calcium bentonite and rare earth solution. Ca-bentonite (20 g) was suspended in REECIO₄ solutions (4.7 × 10⁻² mol dm⁻³). REECIO₄ were prepared by dissolving REE oxides (purchased from Johnson, Matthey & Co., pro anal.). The solutions were shaken for 5 hours, then centrifuged, washed, and dried at room temperature [22].

The preparation method of iron (III)-bentonite is different from the preparation of the rare earth bentonites due to the hydrolysis of iron (III) ions. To minimize the hydrolysis of cations, organic solvents may be applied. For example, iron (III)-montmorillonite can be prepared from acetoneous FeCl₃ solution [25].

For the preparation of iron (III)-bentonite, FeCl₃ (50 g) was solved in acetone while cooling bath was used because of significant solvation heat. After the whole of FeCl₃ was dissolved, a stoichiometric amount of calcium bentonite (based on calcium and iron (III) ions) was added to the FeCl₃ dissolved in acetone. The suspension was stirred on a magnetic stirrer for 1 hour, and it was filtered on a cellulose nitrate filter with 0.45 μm pore size. Then the bentonite was washed with acetone to wash the excess iron (III) ions and air dried at room temperature [26].

The La, Ce, Y, and Fe(III) concentrations of bentonite were determined by X-ray fluorescence analysis (XRF). Instrumental parameters were:

- Si(Li) detector with 20 mm² surface and 3.5 mm evaporated layer (Atomki, Debrecen, Hungary),
- Canberra DSA 1000 digital spectrum analyzer (Canberra Industries, Meriden, CT 06450, USA),
- Canberra Genie 2000 3.0 spectroscopy software (Canberra Industries, Meriden, CT 06450, USA).

The K_α-lines of the lanthanide elements can be excited with 185 MBq 241 Am radioactive source [27].

2.3 Kinetic studies of arsenite (III) sorption on modified bentonites

The arsenite solution was prepared by dissolving As₂O₃ in water and adding 2 g NaOH to the system. Sorption experiments of arsenite ion were carried out by batch technique. 100 mg of cation exchanged bentonite was measured into beakers and 20 cm³ of Na₃AsO₃ solution (5 × 10⁻⁴ mol dm⁻³) was added. All samples were placed

in a Bühler KS15A shaking bath at different temperatures (1, 25, 35, 40 °C) for 2–300 min. After this time, the sorption samples were filtered through a 0.45 µm pore size cellulose nitrate syringe filter and then the concentration in the solution (c_e) was measured by inductively coupled plasma–optical emission spectrometry (ICP–OES) (SPS3 Agilent Technologies 5100). The pH of the solution was measured with a Clean pH200 pH meter and a Clean Cs1030 combined glass electrode. The amount of the sorbed arsenite (III) ions was determined by dividing the difference of the initial ($5 \times 10^{-4} \text{ mol dm}^{-3}$) and the measured arsenite concentration (after the given time) with the mass of bentonite sorbent.

The kinetics of the arsenite (III) sorption was calculated using the software called Scientist. The first-order kinetic model Eq. (1) is:

$$A = A_e (1 - \exp(-kt)) \quad (1)$$

where t is the time, A is the arsenite (III) concentration in bentonite at any time, A_e is the maximum amount of sorbed arsenite (III) on bentonite, k is the first-order rate constant.

2.4 Sorption isotherms of arsenite (III) sorption on La, Ce, Y, Fe(III) modified bentonites

A constant mass of solid (100 mg) was mixed with 20 cm³ solutions containing As(III) concentrations in the range of from 0.0005 to 0.005 mol dm⁻³. Suspensions were shaken for 1 hour, so sorption equilibrium is reached. The additional steps were carried out as in Section 2.3. For X-ray diffraction (XRD) studies (Section 2.6), the solid phase of the sorption experiment with the initial concentration $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_3\text{AsO}_3$ and at 25 °C was prepared. After the sorption and filtration, the solid phase was dried at room temperature and powdered, then it was measured with XRD.

2.4.1 Sorption of arsenic ions from groundwater

La-, Ce-, Y-bentonites were used to sorb arsenic ions from groundwater samples. The groundwater samples were collected in Salonta (Romania). 100 mg modified bentonite was put in 20 cm³ groundwater, then the samples were shaken for 1 hour at 25 °C. After that, the experiment was repeated without mixing, i.e., the samples consisting of 100 mg bentonite and 20 cm³ groundwater, were left at room temperature for 1 day, and the arsenic concentrations (c_e) were measured with ICP–OES, as in Section 2.4.

The basic properties as well as the concentration of dissolved ions of the groundwater are shown in Table 1 and Table 2.

Table 1 Properties and heavy metal content of groundwater from Salonta (Romania)

pH	7.8
conductivity (µS cm ⁻¹)	340
zinc (µg L ⁻¹)	< 20
cadmium (µg L ⁻¹)	< 0.05
chromium (III + VI) (µg L ⁻¹)	< 0.5
copper (mol dm ⁻³)	1.45×10^{-4}
iron (mol dm ⁻³)	1.27×10^{-4}
arsenic (mol dm ⁻³)	6.72×10^{-7}

Table 2 The ion content of groundwater from Salonta (Romania)

Anions (mol dm ⁻³)		Cations (mol dm ⁻³)	
Chloride	2.04×10^{-4}	Calcium	7.14×10^{-4}
Sulfate	2.03×10^{-4}	Magnesium	1.50×10^{-4}
Bicarbonate	4.56×10^{-3}	Potassium	3.94×10^{-5}
Fluoride	1.05×10^{-6}	Sodium	4.06×10^{-3}
Phosphate	2.74×10^{-6}	Lithium	2.13×10^{-5}
		Ammonium	9.98×10^{-6}

2.5 Desorption of arsenite (III) from modified bentonites

These experiments were carried out to determine the desorbed quantity of arsenite (III) ion. Sorption samples were prepared as in the Section 2.4. 100 mg bentonite containing $4.39 \times 10^{-5} \text{ mol g}^{-1}$ arsenite (III) ion were added to 20 cm³ of distilled water. The suspensions were placed in a Bühler KS15A shaking bath at 25 °C. After 1 h, the samples were filtered through a 0.45 µm pore size syringe filter and then c_e was measured with ICP–OES. After filtration, the solid samples were dried at room temperature, powdered, and then were studied with XRD (Section 2.6).

2.6 Determination of d(001) basal spacing of montmorillonite in La, Ce, Y, Fe exchanged bentonites with XRD

The d(001) basal spacing of REE-montmorillonite and that of after sorption and desorption, the preparation of which was written in Section 2.4 and 2.5, were determined with X-ray diffraction (XRD). A Philips PW1710 powder diffractometer equipped with a CuKα source and a graphite

monochromator (operating at 30 mA, 40 kV) was used. The scan rate was $2^\circ 2\theta/\text{min}$.

3 Results and discussion

3.1 La, Ce, Y, and Fe concentrations of bentonite measured by X-ray fluorescence analysis

REE and Fe concentrations measured by X-ray fluorescence analysis are summarized in Table 3. As seen in Table 3, the ion exchange was successful. The REE and Fe(III) ion content in bentonite was higher than CEC values obtained by ammonium acetate method related to trivalent ions ($2.7 \times 10^{-4} \text{ mol g}^{-1}$). This was previously found both for La- and Ce-bentonites and Fe(III)-bentonite by Kovács et al. [27] and Kuzmann et al. [22, 24]. However, in the case of Y-bentonite, this phenomenon was firstly observed here.

Figs. 1-4 show the spectrum of La, Ce, Y and Fe modified bentonites. The red line was highlighted by the Authors for better visibility.

In the case of La, Ce, Y and Fe the centroid of the highest peak area was 33.4 keV, 34.5 keV, 14.9 keV and 6.4 keV, respectively, which are the K_α – line of the elements. The result was analysed by external standard method. The intensity in count per second (cps) was determined by dividing the area of the La-peak with the time. The intensity was used to determine the w/w%, from which the mol/g amount shown in Table 3 was calculated.

3.2 Kinetic studies of arsenite (III) sorption on modified bentonites

Fig. 5 illustrates the sorption of arsenite (III) on lanthanum-modified bentonite. The sorption of arsenite (III) on the La-modified bentonite increases with time. At 1°C , only the equilibrium value was measured, because the kinetics was uncertain. This mechanism is very sensitive to temperature.

In this study the pseudo-first order sorption kinetic equation was used. The pseudo-second order sorption kinetic equation mentioned by Ho and McKay [28]

Table 3 La, Ce, Y, and Fe concentrations of bentonite measured by X-ray fluorescence analysis (XRF)

	La-bentonite	Ce-bentonite	Y-bentonite	Fe-bentonite
XRF (mol g^{-1})	3.50×10^{-4}	2.92×10^{-4}	3.5×10^{-4}	4.85×10^{-4}
REE content related to CEC (%)	130	108	130	179

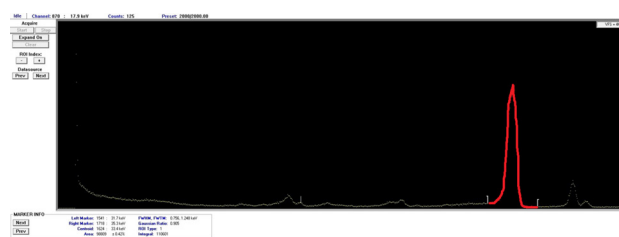


Fig. 1 The spectrum of La-bentonite with XRF

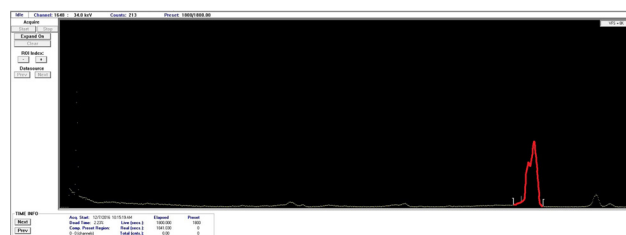


Fig. 2 The spectrum of Ce-bentonite with XRF

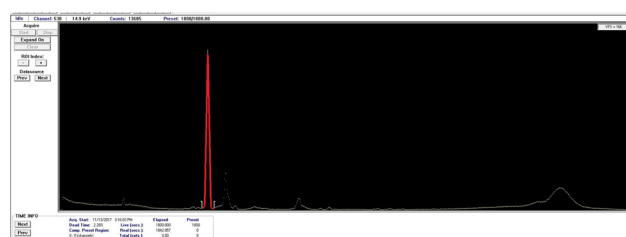


Fig. 3 The spectrum of Y-bentonite with XRF



Fig. 4 The spectrum of Fe-bentonite with XRF

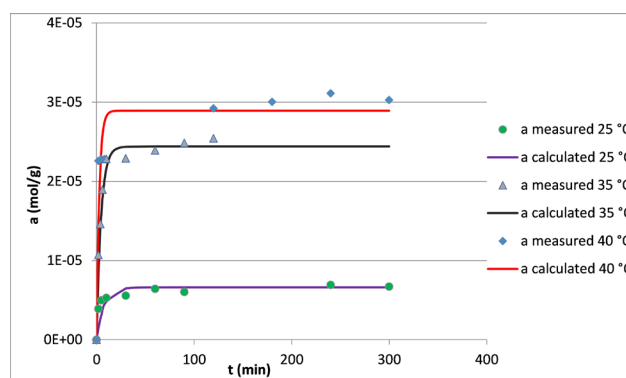


Fig. 5 Arsenite (III) sorption kinetics at 25°C , 35°C and 40°C on lanthanum modified bentonite, 100 mg bentonite, $20 \text{ cm}^3 5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}_3\text{AsO}_3$, pH 7.0–8.43

Table 4 Kinetic parameters at different temperatures on lanthanum modified bentonite (A_e and k was calculated from the Eq. (1))

La-bentonite		
25 °C		
A_e	6.62×10^{-6}	mol g ⁻¹
k	0.15	1 min ⁻¹
pH	7.0-8.03	
SD	1.2×10^{-6}	
R²	0.9636	
35 °C		
A_e	2.44×10^{-5}	mol g ⁻¹
k	0.26	1 min ⁻¹
pH	7.24-8.0	
SD	1.0×10^{-6}	
R²	0.9980	
40 °C		
A_e	2.92×10^{-5}	mol g ⁻¹
k	0.44	1 min ⁻¹
pH	7.7-8.43	
SD	3.8×10^{-6}	
R²	0.9822	

was also tested, R^2 values (25 °C: 0.99; 35 °C: 0.96; 40 °C: 0.98) were better than the pseudo-first order sorption kinetic, but for the activation energy a negative value was obtained which is not a realistic value in reaction kinetics, because the rate is always increases as the temperature increases. Taking these into account in this study the pseudo-first order sorption kinetic equation was used. In the literature, first-order kinetics of As can also be observed for example Singh et al. [29].

The Arrhenius equation (Eq. (2)) was used to determine the activation energy (E_a) of the arsenite (III) sorption. The E_a was obtained by plotting the $\ln(k)$ versus $1/T$.

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (2)$$

where E_a is the activation energy (kJ mol⁻¹), T is the temperature (K), R is the gas constant (8.314 J/K mol), and k_0 is Arrhenius constant.

The calculated E_a value was 53 kJ mol⁻¹, which is higher than the E_a for phosphate sorption in our previous study [30], which was 22 kJ mol⁻¹. Arsenite ion is bigger than phosphate ion, thus arsenite moves slower. It can be supposed that the rate determining step is the diffusion of arsenite ions in the interlayer of montmorillonite [29].

3.3 Sorption isotherms of arsenite (III) ion sorption on La, Ce, Y, Fe modified bentonites

As mentioned in Introduction, arsenic removal methods include precipitation, adsorption, oxidation, and ion exchange. When studying the sorption of arsenite anion on REE and iron (III)-bentonites, the oxidation and ion exchange is excluded. Adsorption and surface precipitation can be supposed.

Adsorption processes are frequently described by Langmuir isotherm model. This isotherm was originally derived for the adsorption of gas molecules on planar surfaces but frequently used in solid / solution systems. The Langmuir equation (Eq. (3)) can be expressed mathematically as follows:

$$\frac{c_e}{a_e} = \frac{c_e}{z} + \frac{K}{z} \quad (3)$$

where a_e is the amount adsorbed at equilibrium (mol g⁻¹), z is the maximum sorption capacity (mol g⁻¹) c_e is the equilibrium solution concentration (mol dm⁻³), and K is the solubility of the sorption complex (mol dm⁻³) [31].

In literature Freundlich and Tempkin isotherm models are also used, but in this study, Langmuir isotherm was used due to all four criterions were supposed to be fulfilled, as follows:

1. The adsorption takes place on the free sites of the adsorbent. The sorption of arsenite (III) ions takes place on free sites produced by the REE cations. It is supposed that in the case of natural calcium-bentonite, no sorption of arsenite ion can be observed.
2. One adsorption site can adsorb one molecule; monolayer coverage is maximum. The arsenite precipitates or adsorbs in the interlayer space on REE ions.
3. The adsorption sites have the same energy (homogeneous surface), no interaction between the adsorbed molecules. It means that the adsorption energy is independent of coverage. As a result of the equivalency of trivalent arsenite and REE ions, the REE-arsenite sorption species are neutral, thus no electrostatic interaction occurs between particles.
4. There is adsorption equilibrium between the phases. Fig. 5 shows that the equilibrium is reached [32].

The isotherm of arsenite (III) sorption on Y-bentonite is illustrated in Fig. 6. For La-, Ce- and Fe-bentonites similar figures were plotted. The isotherm parameters were calculated from the slope of c_e/a_e (g dm⁻³) versus c_e (mol dm⁻³) plots (Table 5).

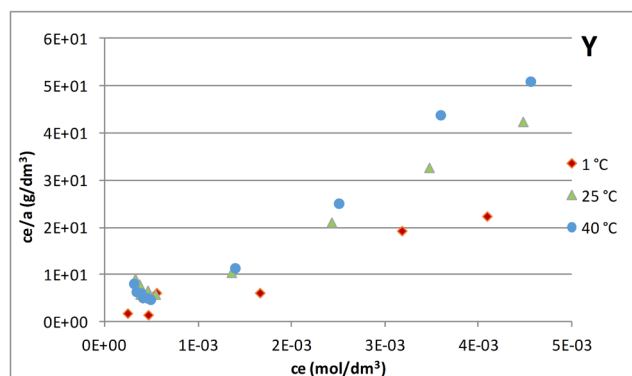


Fig. 6 Arsenite (III) sorption isotherms at 1 °C, 25 °C and 40 °C on yttrium modified bentonite, 100 mg bentonite, 20 cm³ Na₃AsO₃, pH 5.92-10.25

Table 5 Isotherm parameters of arsenite (III) sorption on REE-bentonites

La-bentonite				
<i>T</i>	active sites mol g ⁻¹	SD	solubility mol dm ⁻³	SD
1 °C	1.15 × 10 ⁻⁴	3.54 × 10⁻⁵	1.43 × 10 ⁻³	1.53 × 10⁻⁴
25 °C	1.10 × 10 ⁻⁴	9.19 × 10⁻⁵	1.20 × 10 ⁻³	1.35 × 10⁻⁴
40 °C	1.30 × 10 ⁻⁴	3.54 × 10⁻⁵	8.50 × 10 ⁻⁴	1.38 × 10⁻⁴
Ce-bentonite				
<i>T</i>	active sites mol g ⁻¹	SD	solubility mol dm ⁻³	SD
1 °C	2.60 × 10 ⁻⁴	4.76 × 10⁻⁵	4.30 × 10 ⁻³	1.28 × 10⁻³
25 °C	1.75 × 10 ⁻⁴	9.83 × 10⁻⁵	8.80 × 10 ⁻⁴	1.84 × 10⁻⁵
40 °C	1.60 × 10 ⁻⁴	5.52 × 10⁻⁵	4.80 × 10 ⁻⁴	1.58 × 10⁻⁴
Y-bentonite				
<i>T</i>	active sites mol g ⁻¹	SD	solubility mol dm ⁻³	SD
1 °C	2.60 × 10 ⁻⁴	5.70 × 10⁻⁵	3.70 × 10 ⁻³	3.71 × 10⁻⁴
25 °C	1.15 × 10 ⁻⁴	3.54 × 10⁻⁵	3.60 × 10 ⁻⁴	6.36 × 10⁻⁵
40 °C	1.00 × 10 ⁻⁴	1.77 × 10⁻⁵	1.60 × 10 ⁻⁴	1.34 × 10⁻⁵

As seen in Table 5, La-, Ce- and Y-bentonites can bind similar amount of arsenite (III) ions under the same experimental conditions. The solubilities of the sorption complex (rare earth ion-arsenite-bentonite) decreased with the increasing of temperature. This suggests an exothermic surface sorption process.

The tendencies of solubilities of the complex and active sites versus temperature show the exothermic arsenite sorption reaction. In the absence of literature data for the solubilities of metal - arsenite (III) compounds, the solubility of REE-arsenite-bentonites complex was compared to the solubilities of REE-phosphate-bentonites complexes in our previous study [30]. It can be found that the solubility of the

REE-phosphate-bentonite complex was two orders of magnitude smaller than that of the arsenite complex.

Fe-bentonite cannot bind significant amount of arsenite (III) ions. For Fe-bentonite the error of the results has a large deviation. At 25 °C, the sorbed amount of arsenite (III) on Fe-bentonite is about 5 % sorbed on REE-bentonites. Thus, the values obtained in the case of Fe-bentonite will not be discussed.

In Table 5, the maximum sorption capacity was listed in mol g⁻¹. To compare our results with literature data, these values are given in mg g⁻¹, too. Accordingly, the maximum sorption capacities of La-, Ce-, Y-bentonites for As(III) at 25 °C was 8.24 mg g⁻¹, 13.11 mg g⁻¹, and 8.62 mg g⁻¹, respectively. Lower results were obtained for lanthanum-exchanged zeolite (2.80 × 10⁻³ mg g⁻¹; 2.54 × 10⁻³ mg g⁻¹) [31]. In addition, the maximum sorption capacity of the cerium-loaded cation exchange resin, which was prepared by impregnating cerium into the cation exchange resin, was also lower, 2.53 mg g⁻¹ [34]. Zongliang et al. [34] observed that the value of maximum adsorption capacity for As(III) on cerium-loaded resin decreased with the increasing of temperature which showed the exothermic nature of the sorption process. This is in a good agreement with our findings, that is the active sites in Table 5 decrease as the temperature increases.

3.3.1 Sorption of arsenite ions from groundwater

We wanted to see how REE-bentonites reduce arsenic content in natural water that has other ions than arsenite. Therefore, an experiment was carried out under the same conditions as previous sorption experiments (Section 2.4). Modified (La, Ce, Y) bentonites were used to remove arsenic from groundwater. The initial arsenic concentration of groundwater was 6.72 × 10⁻⁷ mol dm⁻³ (Table 1). After sorption with each modified bentonite, the arsenic concentrations decreased below the detection limit ICP-OES (3.4 × 10⁻⁸ mol dm⁻³ (4 µg/l)). This means that the modified bentonites can sorb arsenic ions from water and can reduce the arsenic concentration in water below the limit determined by the World Health Organization, which is 1.33 × 10⁻⁷ mol dm⁻³ (10 µg l⁻¹).

3.4 Desorption experiments of arsenite (III) on modified bentonites

It is important to regenerate the spent adsorbent and to reuse it in order to the adsorption process be more efficient and more economical. Several studies dealt with the regeneration of clays using NaCl [35], HCl [36, 37],

NH_4Cl [38] and phosphate [39]. In this study, hence the regeneration was tried by desorption after a sorption experiment where the rare earth (La-)bentonite containing $4.39 \times 10^{-5} \text{ mol g}^{-1}$ arsenic. Under the conditions of desorption (Section 2.5), $9.78 \times 10^{-6} \text{ mol g}^{-1}$ was dissolved, $1.22 \times 10^{-5} \text{ mol g}^{-1}$ remained on bentonite, this means the sorbed amount of arsenite (III) was $4.39 \times 10^{-5} \text{ mol g}^{-1}$ and after desorption it was $2.43 \times 10^{-5} \text{ mol g}^{-1}$. The dissolved amount of arsenite (III) was 44.6 %. Therefore, the sorbent can be regenerated. Examination of enhancement and re-use of the sorbents will be carried out.

3.5 Results of d(001) basal spacing of montmorillonite of La, Ce, Y, Fe exchanged bentonites with XRD

Since it was previously assumed that the REE ions in the interlayer space of montmorillonite bind the arsenite ions, it was examined how this can affect the structure, a good indicator of which is the d(001) basal spacing determined by XRD. Table 6, Table 7, and Fig. 7 show the results of XRD used to determine the d(001) basal spacing of REE-montmorillonite and that of after sorption and desorption of arsenite. Desorption experiments were carried out only in the case of La-bentonite.

Table 6 Results of d(001) basal spacing of montmorillonite in La, Ce exchanged bentonites with XRD

	Ca-bentonite	La-bentonite	Ce-bentonite
d(001) basal spacing (nm)	1.4769	1.5159	1.4998
d(001) basal spacing after sorption of arsenite (nm)		1.3916	1.3816
arsenite content after sorption (mol g^{-1})		4.39×10^{-5}	5.37×10^{-5}
d(001) basal spacing after desorption of arsenite (nm)		1.4769	
arsenite content after desorption (mol g^{-1})		2.43×10^{-5}	

Table 7 Results of d(001) basal spacing of montmorillonite in Y, Fe exchanged bentonites with XRD

	Ca-bentonite	Y-bentonite	Fe-bentonite
d(001) basal spacing (nm)	1.4769	1.4769	1.3431
d(001) basal spacing after sorption of arsenite (nm)		1.412	1.2893
arsenite content after sorption (mol g^{-1})		5.71×10^{-5}	2.97×10^{-6}

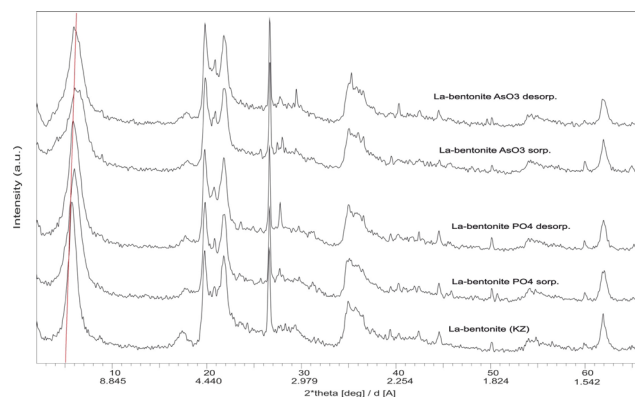


Fig. 7 XRD spectrum of La-bentonite and that of after sorption and desorption of arsenite and phosphate, the unit of y axis is arbitrary unit (a.u.)

The d(001) basal spacing of the original Ca-montmorillonite is 1.4769 nm showing that in the interlayer space there are mostly bivalent calcium ions. As a result with cation exchange with REE ions, an increase in d(001) basal spacing of montmorillonite is observed proving the ion exchange of trivalent REE cations. As mentioned in Section 3.1, the XRF measurements also show the exchange of REE ions.

After the sorption of arsenite ions, the d(001) basal spacing decreases suggesting that the size of the interlayer space decreases, the aluminosilicate layers tend to approach each other. This decrease of d(001) basal spacing may be interpreted by the precipitation reaction of REE cation and arsenite anion in the interlayer space. As a result, the REE cations originally neutralizing the layer charge and reacting with the arsenite ions cannot neutralize the layer charge any more. The negative layer charge, however, must be neutralized by the sodium ions added to the system as the co-ion of arsenite ion, and maybe hydrogen ions. As a result, monovalent sodium ions are in the interlayer space. It is well-known that the d(001) basal spacing of monovalent montmorillonite is less than that of bivalent montmorillonite.

This effect can explain the decrease of the basal spacing. After desorption, an increase in d(001) basal spacing was observed again. This increase, however, is less than of the d(001) basal spacing of La-bentonite before the sorption of arsenite ions and at the same time about 55 % ($2.43 \times 10^{-5} \text{ mol g}^{-1}$) of arsenite ion remains on bentonite. The solubilities of the sorption complex (Table 5), the significant desorption of arsenite by a simple leaching, as well as the changes in the d(001) basal spacing of montmorillonite show that the solubility of montmorillonite-REE-arsenite sorption complex may be rather great. Unfortunately,

we have not found solubility data on REE arsenites, so we cannot compare our result with literature data.

After the sorption of phosphate ions (Fig. 7), the same phenomenon occurs and the cause of the wider peak during arsenite sorption is that arsenite ion is bigger than phosphate ion.

4 Conclusion

Four modified bentonites (La(III), Ce(III), Y(III), and Fe(III)) were prepared for sorption of arsenite ion from aqueous solution. La-, Ce- and Y-bentonites could sorbed arsenite (III) ions, however, iron (III)-bentonite could not.

In equilibrium, the relation between the sorbed and dissolved arsenite concentration can be described by Langmuir isotherm. The experiments at different temperature suggest an exothermic surface precipitation process. After the sorption of arsenit ion on REE exchanged bentonites, the d(001) basal spacing of montmorillonite was decreased

showing the sorption of arsenite ions in the interlayer space. After desorption of arsenite ions by a simple washing, an increase in d(001) was observed again. Desorption experiments show that the significant portion of the sorbed arsenite ions can be leached from rare earth-bentonites, thus the regeneration of the sorbent can be solved.

Arsenite ions could be sorbed by the modified bentonites from natural water containing the usual components of groundwaters.

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